Density Functional Theory and Exchange-Correlation Functionals

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Theory
Biological
Nano
Material

Funding
NSF
NIH
DOE

Izfahan
May 2016
Outline

1. Introduction to the Fundamental Principles of DFT

2. Kohn-Sham Equations and Density Functional Approximations

3. Fractional Perspectives of DFT

The Schrödinger Equation for $N$ electrons

\[ \hat{H} \Psi(x_1, x_2, \ldots x_N) = E \Psi(x_1, x_2, \ldots x_N) \]

\[ x = r, s \]

\[ H = \hat{T} + \hat{V}_{ee} + \sum_{i}^{N} v_{ext}(r_i) \]

\[ \hat{T} = \sum_{i}^{N} -\frac{1}{2} \nabla^2 \]

\[ \hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{r_{ij}} \]

\[ v_{ext}(r) = - \sum_{A}^{Z} \frac{Z_A}{r_{Ai}} \]
**Wavefunction--the curse of dimensionality**

\[ H\Psi = E\Psi \]

<table>
<thead>
<tr>
<th># of electrons</th>
<th>wavefunction</th>
<th>amount of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \Psi(\mathbf{r}_1) )</td>
<td>( 10^3 )</td>
</tr>
<tr>
<td>2</td>
<td>( \Psi(\mathbf{r}_1, \mathbf{r}_2) )</td>
<td>( 10^6 )</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>( N )</td>
<td>( \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) )</td>
<td>( 10^{3N} )</td>
</tr>
</tbody>
</table>

- The amount of data contained in wavefunction grows exponentially with the number of electrons! \( N \sim 1 - 10000 \)

- The problem is caused by the exponential increase in volume associated with adding extra dimensions to a (mathematical) space.
The curse of dimensionality in QM

The problem is caused by the exponential increase in volume associated with adding extra dimensions to a (mathematical) space.
Exponential growth of information

$N$, positions and types of atoms $\iff N, \nu(r)$

$H$

$10^3N$ in $\Psi(r_1, r_2, \ldots r_N)$

1. $\nu(r)$ is the electrostatic potential from the nuclei
2. $\nu(r) = \sum_{Atoms}^{Atoms} \frac{Z_A}{|r - R_A|}$
Electron density $\rho(\mathbf{r})$, 3-dimentional only

Electron density for the hydrogen atom

Electron density for aniline

$$\rho(\mathbf{r}) = \frac{1}{\pi} \exp(-2r)$$

• **Electron density** $\rho(\mathbf{r})$ is the measure of the probability of an electron being present at a specific location.

• Experimental observables in X-ray diffraction for structural determination of small and large molecules
Density Functional Theory

The Nobel Prize in Chemistry 1998

Density functional theory (DFT) (1964, 1965)

1. \( \rho(r) \rightleftharpoons N, \nu(r) \rightleftharpoons \Psi \)

2. \( \rho(r) = \sum_{i} |\phi_{i}(r)|^{2} \) Just the sum of molecular orbital densities
DFT: Exchange-correlation energy

\[ E = E[\rho(\mathbf{r})] \]

\[ E = \text{Kinetic energy} + \text{potential energy} + \text{Coulomb interaction energy} + E_{xc}[\rho(\mathbf{r})] \]

\[ E_{xc}[\rho(\mathbf{r})] \]

- Exchange-correlation energy
- The only unknown piece in the energy
- About 10% of \( E \)
Approximations in exchange-correlation energy

\[ E_{xc}[\rho(r)] \]

- 1965: Kohn and Sham, Local Density Approximation (LDA)
- 1980s-1990s: Axel Becke, Robert Parr, John Perdew
- Generalized Gradient Approximation (GGA)
- Hybrid Functionals (B3LYP, PBE0)
Density Functional Theory

- Structure of matter: atom, molecule, nano, condensed matter
- Chemical and biological functions
- Electronic
- Vibrational
- Magnetic
- Optical (TD-DFT)
ISI Web of Science search for articles with topic “density functional theory”

103573 DFT records, March 2014
A deeper look at the Hamiltonian

\[ H = \hat{T} + \hat{V}_{\text{ee}} + \sum_{i} v_{\text{ext}}(r_i) \]

Only \( \sum_{i} v_{\text{ext}}(r_i) \) depends on atoms and molecules

\[ \sum_{i}^{N} v_{\text{ext}}(r_i) = \int dr v_{\text{ext}}(r) \sum_{i}^{N} \delta(r - r_i) \]

\[ \int dr f(r) \delta(r - r_0) = f(r_0) \]
Introducing the electron density

\[ \langle \Psi \mid \sum_{i}^{N} v_{\text{ext}}(\mathbf{r}_i) \mid \Psi \rangle = \int d\mathbf{x}^{N} |\Psi(x_1, x_2, \ldots x_N)|^{2} \sum_{i}^{N} v_{\text{ext}}(\mathbf{r}_i) \]

\[ = \int d\mathbf{x}^{N} |\Psi(x_1, x_2, \ldots x_N)|^{2} \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \]

\[ = \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \int d\mathbf{x}^{N} |\Psi(x_1, x_2, \ldots x_N)|^{2} \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \]

\[ = \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \]
Introducing the electron density

\[
\rho(\mathbf{r}) = \int d\mathbf{x}^N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \sum_{i} \delta(\mathbf{r} - \mathbf{r}_i)
\]

\[
= \langle \Psi | \sum_{i} \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle
\]

\[
= N \langle \Psi | \delta(\mathbf{r} - \mathbf{r}_1) | \Psi \rangle
\]

\[
= N \int d\mathbf{x}^N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \delta(\mathbf{r} - \mathbf{r}_1)
\]

\[
= N \int ds_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N |\Psi(r s_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2
\]
1. The electron density at \( r \) in physical space

2. The probability of finding an electron at \( r \)

3. A function of three variables

\[
\rho(r) \geq 0
\]

\[
\int d\mathbf{r} \rho(r) = N
\]
For a determinant wave function

\[ |\Phi_0\rangle = |\chi_1\chi_2\cdots\chi_i\chi_j\cdots\chi_N\rangle \]

\[ \rho(r) = \langle \Phi_0 | \sum_i \delta(r - r_i) |\Phi_0\rangle \]

\[ = \sum_i \langle \Phi_0 | \delta(r - r_i) |\Phi_0\rangle \]

\[ = \sum_i \int dx_i |\chi_i(x_i)|^2 \delta(r - r_i) \]

\[ = \sum_i \int dx_i |\chi_i(x_i)|^2 \delta(r - r_i) \]

\[ = \sum_i \int dr_i \sum_{s_i} |\phi_i(r_i)\sigma(s_i)|^2 \delta(r - r_i) \]

\[ = \sum_i |\phi_i(r)|^2 \]
The variational principle for ground states

\[ E^0 = \min_{\Psi} \langle \Psi | H | \Psi \rangle \]

\[ = \min_{\Psi} \left\{ \langle \Psi | T + V_{ee} | \Psi \rangle + \langle \Psi | \sum_{i}^{N} v_{ext}(r_i) | \Psi \rangle \right\} \]

\[ = \min_{\Psi} \left\{ \langle \Psi | T + V_{ee} | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \]

Most QM methods use the wavefunction as the computational variable and work on its optimization.
An alternative route

Goal: Looking for the max height, and the tallest kid in a school.

1) We can first look for the tallest kid in each class
2) then compare the result from each class
An alternative route

Goal: Looking for the max height, and the tallest kid in a school.

1) We can first look for the tallest kid in each class
2) then compare the result from each class

\( h(K_i) \) is the height of kid \( K_i \)

\[
\text{max height} = \max_i \{h(K_i)\}
\]

\[
= \max_J \max_{K_i \in \text{class}(J)} \{h(K_i)\}
\]

\[
= \max_J H(J)
\]

\( H(J) = \max_{K_i \in \text{class}(J)} \{h(K_i)\} \), the max height of class \( J \)
An alternative route

\[
\begin{align*}
\max \text{ height} & = \max_i \{h(K_i)\} \\
& = \max_J \max_{K_i \in \text{class}(J)} \{h(K_i)\} \\
& = \max_J H(J)
\end{align*}
\]

- \(i\) is the original variable

- \(J\) is the reduced variable

\(H(J) = \max_{K_i \in \text{class}(J)} \{h(K_i)\}\) is a constrained search
The constrained-search formulation of DFT

\[ E^0 = \min_{\Psi} \left\{ \langle \Psi | T + V_{ee} | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \]

\[ = \min_{\rho(\mathbf{r})} \min_{\Psi \to \rho(\mathbf{r})} \left\{ \langle \Psi | T + V_{ee} | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \]

\[ = \min_{\rho(\mathbf{r})} \left\{ \min_{\Psi \to \rho(\mathbf{r})} \langle \Psi | T + V_{ee} | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \]

\[ = \min_{\rho(\mathbf{r})} \left\{ F[\rho(\mathbf{r})] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \]

\[ = \min_{\rho(\mathbf{r})} E_v[\rho(\mathbf{r})] \]

Levy, 1979
The constrained search

A. We have a new $F[\rho(r)] = \min_{\Psi \to \rho(r)} \langle \Psi | T + V_{ee} | \Psi \rangle$

1. A functional of density; given a density, it gives a number.
2. A universal functional of density, independent of atoms, or molecules.

B. The ground state energy is the minimum

$$E^0 = \min_{\rho(r)} E_v[\rho(r)]$$

$$= \min_{\rho(r)} \left\{ F[\rho(r)] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\}$$

C. $\rho(\mathbf{r})$ is the new reduced variable
The condition on the density

\[ F[\rho(r)] = \min_{\Psi \rightarrow \rho(r)} \langle \Psi | T + V_{ee} | \Psi \rangle \]

For what density the energy functional is defined?

-- It has to come from some wavefunction, N-representable

-- the N-representability is insured if

\[ \rho(r) \geq 0 \]

\[ \int d\mathbf{r} \rho(\mathbf{r}) = N \]

\[ \int d\mathbf{r} |\nabla \rho(\mathbf{r})|^2 < \infty \]
The Thomas Fermi Approximation for $T$

1. Divide the space into many small cubes

2. Approximate the electrons in each cubes as independent particles in a box (Fermions)

3. $T = \text{Sum of the contributions from all the cubes}$

Eigenstate energies for particle in a cubic box

$$\epsilon = \frac{\hbar^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2}{8ml^2} R^2_\epsilon$$

With quantum numbers $n_x, n_y, n_z = 1, 2, 3, \ldots$

Each state can have two electrons (spin up and spin down).
The number of states (with energy \( < \epsilon \) \( \Phi(\epsilon) \))

\[
\Phi(\epsilon) = \frac{1}{8} \frac{4\pi R^3_\epsilon}{3} = \frac{\pi}{6} \left( \frac{8ml^2}{h^2} \right)^\frac{3}{2} \epsilon
\]

Density of states

\[
g(\epsilon) = \frac{d\Phi(\epsilon)}{d\epsilon} = \frac{\pi}{4} \left( \frac{8ml^2}{h^2} \right)^\frac{3}{2} \epsilon
\]

Two electrons occupy each state. The kinetic energy is

\[
t = 2 \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon = \frac{8\pi}{5} \left( \frac{2m}{h^2} \right)^\frac{3}{2} l^3 \epsilon^\frac{5}{2}_F
\]

\[
N = 2 \int_0^{\epsilon_F} g(\epsilon) d\epsilon = \frac{8\pi}{3} \left( \frac{2m}{h^2} \right)^\frac{3}{2} l^3 \epsilon^\frac{3}{2}_F
\]
The Thomas Fermi Approximation for $T$

To express $t$ as a function of density

$$t = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} l^3 \left( \frac{N}{l^3} \right)^{\frac{5}{3}}$$

$$\frac{N}{l^3} \to \rho$$

$$l^3 \to dr$$

$$T_{TF}[\rho] = \sum t = C_F \int dr \rho(r)^{\frac{5}{3}}$$

$$C_F = \frac{3}{10} (3\pi^2)^{\frac{2}{3}}$$

--- Local density approximation for $T$
The Thomas Fermi energy functional

For the Vee functional, use the classical electron-electron interaction energy

\[ J[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \]

The Thomas-Fermi total energy functional is

\[ E_{TF}[\rho] = C_F \int d\mathbf{r} \rho(\mathbf{r})^{\frac{5}{3}} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \]

The minimization of \( E_{TF}[\rho] \) leads to the Euler-Lagrange equation, with \( \mu \) for the constraint of \( \int d\mathbf{r} \rho(\mathbf{r}) = N \).

\[ \mu = \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_{TF}[\rho]}{\delta \rho(\mathbf{r})} + v_J(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) \]

or

\[ \frac{5}{3} C_F \rho(\mathbf{r})^{\frac{5}{3}} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{ext}}(\mathbf{r}) = \mu \]
Adding the local approximation to the exchange energy

**Dirac exchange energy functional**

\[ E_{x}^{LDA}[\rho] = -C_D \int \rho(\mathbf{r})^{\frac{4}{3}} d\mathbf{r} \]

Slater, Gaspar, the \( X\alpha \) approximation

\[ E_{x}^{X\alpha}[\rho] = -\frac{3}{2} \alpha C_D \int \rho(\mathbf{r})^{\frac{4}{3}} d\mathbf{r} \]

\[ C_D = \frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \]
1 Question to the students

In 3d

\[ T_{TF}[\rho] = C_F \int d\mathbf{r} \rho(\mathbf{r})^{\frac{5}{3}} \]

\[ C_F = \frac{3}{10} \left(3\pi^2\right)^{\frac{2}{3}} \]

What is the Thomas–Fermi kinetic energy functional in 2 dimensional space?
Comments on TF theory

• Beautiful and simple theory, with density as the basic variable

BUT,  
• the energy is NOT a bound to the exact energy  
• no shell structure for atoms, no quantum oscillation  
• no bounding for molecules

• Main problem is in the local approximation for T
2. Kohn-Sham Theory and Density Functional Approximations

• Kohn-Sham equations
• Generalized Kohn-Sham equations
• Exchange and correlation energy functional
• Adiabatic Connections
• Density Functional Approximations
Kohn-Sham theory, going beyond the Thomas-Fermi Approximation

Use a non-interacting electron system, —Kohn-Sham reference system, to calculate the electron density and kinetic energy

$$|\Phi_s\rangle = |\chi_1 \chi_2 \cdots \chi_i \chi_j \cdots \chi_N\rangle$$

$$\rho(r) = \sum_i |\phi_i(r)|^2$$

$$T_s[\rho] = \langle \Phi_s | \sum_i -\frac{1}{2} \nabla_i^2 |\Phi_s\rangle$$

$$= \sum_i \int d\mathbf{r}_i \phi_i^*(\mathbf{r}_i) \left( -\frac{1}{2} \nabla_i^2 \right) \phi_i(\mathbf{r}_i)$$

$$= \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 |\phi_i\rangle$$
Kohn-Sham theory

\[ \rho(\mathbf{r}) = \sum_{i}^{N} |\phi_i(\mathbf{r})|^2 \]  \hspace{1cm}  \[ T_s[\rho] = \sum_{i}^{N} \langle \phi_i | - \frac{1}{2} \nabla^2 | \phi_i \rangle \]

- \( \rho(\mathbf{r}) = \sum_{i} |\phi_i(\mathbf{r})|^2 \) is the true electron density, but \( T_s[\rho] \) is not \( T[\rho] \). However, \( T_s[\rho] \) is a very good approximation to \( T_s[\rho] \)

- The essence of KS theory is to solve \( T_s[\rho] \) exactly in terms of orbitals.
Kohn-Sham theory

\[ \rho(\mathbf{r}) = \sum_{i}^{N} |\phi_i(\mathbf{r})|^2 \quad \quad T_s[\rho] = \sum_{i}^{N} \langle \phi_i | - \frac{1}{2} \nabla^2 | \phi_i \rangle \]

Introduce the exchange correlation energy functional

\[ F[\rho] = T[\rho] + V_{ee}[\rho] \]
\[ = T_s[\rho] + J[\rho] + E_{xc}[\rho] \]

\[ E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \]

\[ J[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \]
\[ \rho(\mathbf{r}) = \sum_{i} \left| \phi_i(\mathbf{r}) \right|^2 \quad \text{and} \quad T_s[\rho] = \sum_{i} \langle \phi_i \rangle - \frac{1}{2} \nabla^2 \langle \phi_i \rangle \]

In terms of the orbitals, the KS total energy functional is now

\[ E_v[\rho] = \sum_{i} \langle \phi_i \rangle - \frac{1}{2} \nabla^2 \langle \phi_i \rangle + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \]

The g.s. energy is the minimum of the functional w.r.t. all possible densities. The minimum can be attained by searching all possible orbitals

\[ W[\phi_i] = E_v[\phi_i] - \sum_{i} \varepsilon_i \{ \langle \phi_i | \phi_i \rangle - 1 \} \]

\[ \frac{\delta W[\phi_i]}{\delta \phi_i(\mathbf{r})} = 0 \]
\[ W[\phi_i] = E_v[\phi_i] - \sum_i^N \varepsilon_i \{\phi_i | \phi_i \} - 1 \]
\[ \frac{\delta W[\phi_i]}{\delta \phi_i(r)} = 0 \]

The orbitals \{\ket{\phi_i}\} are the eigenstates of an one-electron local potential \( \nu_s(r) \) if we have explicit density functional for \( E_{xc}[\rho] \) (KS equations)

\[ \left( -\frac{1}{2}\nabla^2 + \nu_s(r) \right) \ket{\phi_i} = \varepsilon_i \ket{\phi_i}, \]

or a nonlocal potential \( \nu_s^{NL}(r,r') \), if we have orbital functionals for \( E_{xc}[\phi_i] \) (generalized KS equations)

\[ \left( -\frac{1}{2}\nabla^2 + \nu_s^{NL}(r,r') \right) \ket{\phi_i} = \varepsilon_i^{GKS} \ket{\phi_i}. \]
One electron Equations

Kohn-Sham (KS)

\[
\left( -\frac{1}{2}\nabla^2 + v_s(r) \right) |\phi_i\rangle = \varepsilon_i |\phi_i\rangle,
\]

\[
v_s(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} + v_J(r) + v_{ext}(r)
\]

Generalized Kohn-Sham (GKS)

\[
\left( -\frac{1}{2}\nabla^2 + v_s^{NL}(r,r') \right) |\phi_i\rangle = \varepsilon_i^{GKS} |\phi_i\rangle.
\]

\[
v_s^{NL}(r,r') = \frac{\delta E_{xc}[\delta \rho_s(r', r)]}{\delta \rho_s(r', r)} + [v_J(r) + v_{ext}(r)] \delta(r' - r)
\]
1. With N orbitals, the kinetic energy is treated rigorously. In comparison with the Thomas-Fermi theory in terms of density, it is a trade of computational difficulty for accuracy.

2. The KS or GKS equations are in the similar form as the Hartree-Fock equations and can be solved with similar efforts.

3. KS or GKS changes a N interacting electron problem into an N non-interacting electrons in an effective potential.

4. The E_xc is not known, explicitly. It is about 10% of the energy for atoms.
Adiabatic connection: from Kohn-Sham reference system to the true physical system

\[ F[\rho] = T[\rho] + V_{ee}[\rho] \]
\[ = T_s[\rho] + J[\rho] + E_{xc}[\rho] \]

So far, the \( E_{xc} \) is expressed in a form that is not appealing, not revealing, not inspiring…

\[ E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \]

What is the relation of the Kohn-Sham reference system to the true physical system?

- The same electron density

\[ \rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \]

- Anything else?
Adiabatic connection: from Kohn-Sham reference system to the true physical system

\[ \rho(\mathbf{r}) = \sum_{i}^{N} |\phi_{i}(\mathbf{r})|^{2} \]

<table>
<thead>
<tr>
<th></th>
<th>Kohn-Sham Reference System</th>
<th>Physical System</th>
</tr>
</thead>
<tbody>
<tr>
<td>the same (\rho(\mathbf{r}))</td>
<td>(\sum_{i} n_{i}</td>
<td>\phi_{i}(\mathbf{r})</td>
</tr>
<tr>
<td>Hamiltonian</td>
<td>(H_{s} = \sum_{j}^{N} h_{s}(j) = \sum_{j}^{N} -\frac{1}{2} \nabla_{j}^{2} + v_{s}(\mathbf{r}_{j}))</td>
<td>(H = \hat{T} + \hat{V}<em>{ee} + \sum</em>{i}^{N} v_{\text{ext}}(\mathbf{r}_{i}))</td>
</tr>
<tr>
<td>Energy</td>
<td>(E_{s} = \langle \Psi_{s}</td>
<td>H_{s}</td>
</tr>
<tr>
<td></td>
<td>(E_{s} = T_{s}[\rho] + \int d\mathbf{r} v_{s}(\mathbf{r})\rho(\mathbf{r}))</td>
<td>(E = T_{s}[\rho] + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}))</td>
</tr>
<tr>
<td>connecting (H_{\lambda})</td>
<td>(\sum_{j}^{N} -\frac{1}{2} \nabla_{j}^{2} + \lambda \hat{V}<em>{ee} + \sum</em>{i}^{N} v_{\lambda}(\mathbf{r}<em>{i})), keeping fixed density (\rho</em>{\lambda}(\mathbf{r}) = \rho(\mathbf{r}))</td>
<td>(H_{0} = H_{s})</td>
</tr>
<tr>
<td></td>
<td>(H_{1} = H)</td>
<td></td>
</tr>
</tbody>
</table>
Adiabatic connection: from Kohn-Sham reference system to the true physical system

\[ E_{xc}[\rho] = \int_0^1 \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle \ d\lambda - J[\rho] \]

- Exc in terms of wavefunction!
- Compared with
  \[ E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \]
- What is the integrand at \( \lambda = 0 \) ?
- Starting point to make approximations – DFA (Density functional approximation)
The Local Density Approximation (Kohn-Sham, 1964)

\[ E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})) \]

\( \varepsilon_{xc}(\rho(\mathbf{r})) \) is the XC energy per particle of a homogeneous electron gas of density \( \rho \). It is a function of \( \rho \).

Dirac exchange energy functional

\[ E_{x}^{LDA}[\rho] = -C_D \int \rho(\mathbf{r})^{\frac{4}{3}} d\mathbf{r} \]
Beyond the Local Density Approximation

\[ E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})) \]

<table>
<thead>
<tr>
<th>Method</th>
<th>Expression</th>
<th>Functionals</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>( E_{xc} = \int d\mathbf{r} f(\rho) )</td>
<td>VWN, PW,</td>
</tr>
<tr>
<td>GGA</td>
<td>( E_{xc} = \int d\mathbf{r} f(\rho, \nabla \rho) )</td>
<td>BLYP, PW96, PBE</td>
</tr>
<tr>
<td>Hybrid</td>
<td>( E_{xc} = c_1 E_{HF} + c_2 E_{xc}^{GGA} )</td>
<td>B3LYP, PBE0</td>
</tr>
<tr>
<td>range-separated</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ E_x^{\text{B88}} = - \sum_{\sigma = \alpha, \beta} \int \rho_\sigma^{4/3} \left[ \frac{3}{4} \left( \frac{6}{\pi} \right)^{1/3} + \frac{\beta x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma} \right] \, dr \]

\[ E_x^{\text{PBE}} = - \int \rho^{4/3} \left[ \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} + \frac{\mu s^2}{1 + \mu s^2 / \kappa} \right] \, dr \]

\[ E_x^{\text{HF}} = - \frac{1}{2} \sum \int \int \frac{\phi^*_{i\sigma}(r) \phi_{j\sigma}(r) \phi^*_{j\sigma}(r') \phi_{i\sigma}(r')}{|r - r'|} \, dr \, dr' \]

\[ E_{xc}^{\text{B3LYP}} = 0.2E_x^{\text{HF}} + 0.8E_x^{\text{LDA}} + 0.72\Delta E_x^{\text{B88}} + 0.81E_c^{\text{LYP}} + 0.19E_c^{\text{VWN}} \]
Atomization energies for a few selected molecules, mH

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Exp.</th>
<th>LSDA</th>
<th>PBE</th>
<th>UHF</th>
<th>MP2</th>
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<td>H₂</td>
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<td>31.7</td>
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<td>Be₂</td>
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<td>87.8</td>
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Mean Absolute Errors (MAE) Thermochemistry (G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities

<table>
<thead>
<tr>
<th>functional</th>
<th>post-B3LYP</th>
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<tr>
<td></td>
<td>G3</td>
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<tr>
<td></td>
<td>(kcal/mol)</td>
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<tr>
<td>LDA</td>
<td>72.24</td>
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GGA and Meta-GGA

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<td>functional</td>
<td>post-B3LYP</td>
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<tr>
<td>------------</td>
<td>------------</td>
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<tr>
<td></td>
<td>G3 (kcal/mol)</td>
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<tr>
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<td>HFLYP</td>
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**Hybrid Functionals**
Mean Absolute Errors (MAE) Thermochemistry (G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities

<table>
<thead>
<tr>
<th>functional</th>
<th>G3 (kcal/mol)</th>
<th>barriers- (kcal/mol)</th>
<th>T96 ((a_0))</th>
<th>H bond- (kcal/mol)</th>
<th>(\alpha_{iso}) (au)</th>
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<tbody>
<tr>
<td>LDA</td>
<td>72.24</td>
<td>14.36</td>
<td>0.0107</td>
<td>3.02</td>
<td>0.78</td>
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</table>

| Range-Separated Functionals |
|-----------------------------|----------------|----------------|----------------|-----------------|----------------|
| CAMB3LYP                    | 4.04           | 2.51           | 0.0119         | 0.69            | 0.23            |
| LCBLYP                      | 16.91          | 3.73           | 0.0169         | 0.90            | 0.31            |
| rCAMB3LYP                   | 5.50           | 2.76           | 0.0225         | 0.78            | 0.37            |
| LC-PBE                      | 16.69          | 3.07           | 0.0245         | 0.75            | 0.53            |
| HSE                         | 4.37           | 3.43           | 0.0082         | 0.77            | 0.21            |
A large class of problems

- Wrong dissociation limit for molecules and ions
- Over-binding of charge transfer complex
- too low reaction barriers
- Overestimation of polarizabilities and hyperpolarizabilities
- Overestimation of molecular conductance in molecular electronics
- Incorrect long-range behavior of the exchange-correlation potential
- Charge-transfer excited states
- Band gaps too small
- Diels-Alder reactions, highly branched alkanes, dimerization of aluminum complexes
Error Increases for systems with fractional number of electrons: Yingkai Zhang and WY, JCP 1998

\[ \text{H}_2^+ \] at the dissociation limit

too low energy for delocalized electrons

\[ \text{H}_2^+ \] at the dissociation limit

too low energy for delocalized electrons

Savin, in Seminario, “Recent Developments and Applications of Modern DFT”, 1996
DFT for fractional number of electrons from grand ensembles,
Perdew, Parr, Levy, and Balduz, PRL. 1982

\[ E_{N+\delta} = (1 - \delta)E_N + \delta E_{N+1} \]
\[ \rho_{N+\delta} = (1 - \delta)\rho_N + \delta \rho_{N+1} \]
Where can you find fractional charges?

\( \text{WY, Yingkai Zhang and Paul Ayers, PRL, 2000 – pure states} \)

\[ H_2^+ \text{ at the dissociation limit} \]

\[ \Psi_\alpha \]
\[ E_\alpha = E(0) + E(1) \]

\[ \Psi_\beta \]
\[ E_\beta = E(1) + E(0) \]

\[ \Psi_\gamma = \frac{1}{\sqrt{2}} \left( \Psi_\alpha + \Psi_\beta \right) \]
\[ E_\gamma = E(\frac{1}{2}) + E(\frac{1}{2}) = 2E(\frac{1}{2}) \]

\[ E(N): \quad E(\frac{1}{2}) = \frac{1}{2} E(0) + \frac{1}{2} E(1) = \frac{1}{2} E(1) \]
The linearity condition in fractional charges: The energy $E(e/2)$ is given by:

$$E(e/2) = \frac{1}{2} E(1)$$
$E(N)$
A dimer, with ∞ separation: each monomer has $E(N)$

For $\delta N$-convex, $2E(N + \frac{1}{2}) < E(N) + E(N + 1)$, delocalized

For $\delta N$-concave, $2E(N + \frac{1}{2}) > E(N) + E(N + 1)$, localized
Consequence of Delocalization Error

1. predicts too low energy for delocalized distributions

2. gives too delocalized charge distributions
Define the **Delocalization Error** as the violation of the linearity condition for fractional charges.
Delocalization Error vs. Self-Interaction Error (SIE)

SIE (Perdew-Zunger 1982)

- Exc error for one-electron systems
- Self-Interaction Correction (SIC) forces the correction for every one-electron orbital, improves atomic systems.
- SIC does not improve molecular systems in general (kind over corrections).
- SIC fractional extension (0<N<1, Zhang and Yang, JCP 1998) explained $H_2^+$ problem

Delocalization Error (Mori-Sanchez, Cohen and Yang, PRL 2008)

- Two SIE-free functionals: Becke06, and MCY2 (2006) did not solve the problems (Self-interaction-free exchange-correlation functional for thermochemistry and kinetics, Mori-Sanchez, Cohen and Yang, JCP 2006)
- Many-electron SIE were used in 2006 (Mori-Sanchez, Cohen and Yang, JCP 2006, A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, JCP 2007)
- Delocalization Error agrees with SIE for one electron systems. For general systems, it reveals the true relevant mathematical error of approximate functionals, and captures the physical nature of the error—delocalization.
Too low energy for fractional charge systems

- Energy of dissociation of molecular ion: too low
- Charge transfer complex energy: too low
- Transition state energy: too low
- Charge transfer excitation energy: too low
- Band gap: too low
- Molecular conductance: too high
- (Hyper)polarizability for long molecules: too high
- Diels-Alder reaction products, highly branched alkanes, dimerization of aluminum complexes: too high

Cohen, Mori-Sanchez and Yang, 2008 Science
Seeing the delocalization error

$\text{Cl}^- (\text{H}_2\text{O})_7$

Where is the negative charge?
Another large class of problems

- huge error dissociation of chemical bonds
- transition metal dimmers
- some magnetic properties
- strongly correlated systems
- Mott insulators, high $T_c$ superconductors
- degeneracy and near degeneracy

Static Correlation Error
The huge error in breaking any bond
Where can you find fractional spins?

Aron Cohen, Paula Mori-Sanchez and Yang, 2008, JCP
Yang, Ayers and Zhang, PRL 2000

\[ \Psi_\alpha \]
\[ E_\alpha = E(\downarrow) + E(\uparrow) \]

\[ \Psi_\beta \]
\[ E_\beta = E(\uparrow) + E(\downarrow) \]

\[ \Psi_\gamma = \frac{1}{\sqrt{2}}(\Psi_\alpha + \Psi_\beta) \]
\[ E_\gamma = 2E(\uparrow) = 2E(\downarrow) \]

Fractional Spin H Atom: half spin up electron and half spin down electron

\[ E \left( \frac{\uparrow \downarrow}{2} \right) = E(\uparrow) = E(\downarrow) \]
The constancy condition: energy of fractional spins

\[ E(\gamma) = \frac{E(\uparrow \downarrow)}{2} = E(\uparrow) = E(\downarrow) \]
Define the **Static Correlation Error** as the violation of the constancy condition for fractional spins.

*C* 

**H₂ binding curve**

```
R (Angstrom)
```

- **Cohen, Mori-Sanchez and Yang, 2008, JCP; 2008 Science**
Why we have to deal with fractional number of electrons?

\[ \rho(r) \leftrightarrow \Psi(r_1, r_2, \ldots r_N) \]

\[ E = E[\rho(r)] \]

Density Functional Theory

Fractional charge can occur

Many-electron theories based on
• Green function
• Density matrix

\[ E = \langle \Psi | H | \Psi \rangle \]

Wavefunction Theory

Integers, always!
Exact conditions on DFT

**Fractional Charge:** 1982: Perdew, Levy, Parr and Baldus

\[
E[(1 - \delta)\rho_N + \delta\rho_{N+1}] = (1 - \delta)E_N + \delta E_{N+1}
\]

**Fractional Spins:** 2000, PRL, WY, Zhang and Ayers;
2008, JCP, Cohen, Moris-Sanchez, and WY

\[
E\left[\sum_i c_i \rho_{N,i}\right] = E[\rho_{N,i}] = E_N
\]

**Fractional Charges and Spins:** 2009: PRL, Moris-Sanchez, Cohen and WY

\[
E\left[(1 - \delta)\sum_i c_i \rho_{N,i} + \delta \sum_j d_j \rho_{N+1,j}\right] = (1 - \delta)E_N + \delta E_{N+1}
\]

•!! The exact XC functional cannot be an explicit and differentiable functional of the electron density/density matrix, either local or nonlocal.

•Valid for density functionals, and also for 1-body density matrix functionals, 2-RDM theory, and other many-body theories.
Falt – plan for Hydrogen: $H^+, H, and H^-$

Fractional Charge and Fractional Spin Combined

$\alpha = \beta$

Fractional Charges and Spins: PRL 2009, Cohen, Moris-Sanchez, and WY
Band Gap

Definition of fundamental gap

\[ E_{\text{gap}}^{\text{integer}} = \{ E(N - 1) - E(N) \} - \{ E(N) - E(N + 1) \} \]
\[ = I - A \]

\[ E_{\text{gap}}^{\text{deriv}} = \left\{ \frac{\partial E}{\partial N} \bigg|_{N+\delta} - \frac{\partial E}{\partial N} \bigg|_{N-\delta} \right\} \]

\[ E_{\text{gap}}^{\text{integer}} = E_{\text{gap}}^{\text{deriv}}, \text{ Only if } E(N + \delta) \text{ is linear.} \]
How can fundamental gap be predicted in DFT

• **LUMO** energy is the chemical potential for electron addition

• **HOMO** is the chemical potential for electron removal

• **Fundamental gaps** predicted from DFT with KS, or GKS calculations, as the KS gap or the GKS gap

• For **orbital functionals**, the LUMO of the KS (OEP) eigenvalue is NOT the chemical potential of electron addition.

Thus the KS gap is not the fundamental gap predicted by the functional.

\[
\frac{\partial E_v(N)}{\partial N} = \langle \phi_f | H_{\text{eff}} | \phi_f \rangle
\]

WY, Mori-Sanchez and Cohen, PRB 2008, JCP 2012
For Linear $E(N)$

$$\Delta N = 1, \quad \Delta E = \frac{\partial E}{\partial N}$$

Convex curve (LDA, GGA):
- derivative underestimates I, overestimates A, \text{ I-A is too small }

Concave curve (HF):
- derivative overestimates I, underestimate A, \text{ I-A is too large }
How well can fundamental gap be predicted in DFT

- **Fundamental gaps** predicted from DFT with KS, or GKS calculations, as the KS gap or the GKS gap

- Only works well if functionals have minimal delocalization/localization error.
Improving band gap prediction in density functional theory from molecules to solids

PRL, 2011, Xiao Zheng, Aron J. Cohen, Paula Mori-Sanchez, Xiangqian Hu, and Weitao Yang

Xiao Zheng (USTC)
Aron J. Cohen (Cambridge)
Paula Mori-Sanchez (Univ. Autonoma Madrid)
Xiangqiang Hu
Nonempirical Scaling correction

To linearize an energy component, $E_{\text{comp}}$, for a system of $N + n$ ($0 < n < 1$) electrons, we construct

$$\tilde{E}_{\text{comp}}(N + n) = (1 - n)E_{\text{comp}}(N) + nE_{\text{comp}}(N + 1)$$

$\tilde{E}_{\text{comp}}(N + n)$ scales linearly with $n$, and reproduces $E_{\text{comp}}$ at $n = 0$ and $n = 1$.

The SC to $E_{\text{comp}}$ is

$$\Delta E_{\text{comp}}(N + n) = \tilde{E}_{\text{comp}}(N + n) - E_{\text{comp}}(N + n)$$

It is then important to cast $\Delta E_{\text{comp}}$ into a functional form, so that it depends explicitly on $\rho(r)$, or on Kohn-Sham first-order reduced density matrix $\rho_s(r, r')$. 
Energy versus fractional electron number

The SC significantly restores linearity condition for energy
Summary of band-gap prediction for a variety of systems

<table>
<thead>
<tr>
<th>eV</th>
<th>MAE (# of data)</th>
<th>MLDA</th>
<th>S-MLDA</th>
<th>LDA</th>
<th>S-LDA</th>
<th>B3LYP</th>
<th>S-B3LYP</th>
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<tr>
<td>I (18)</td>
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<td>0.16</td>
<td>0.16</td>
<td>0.30</td>
<td>0.30</td>
<td>0.20</td>
<td>0.20</td>
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<tr>
<td>A (15)</td>
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<td>0.25</td>
<td>0.27</td>
<td>0.27</td>
<td>0.12</td>
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<td>$\epsilon_{\text{HOMO}}$ (18)</td>
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<td>5.18</td>
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<td>3.88</td>
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<td>$I_{\text{ad}}$ (70)</td>
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<td>0.16</td>
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<td>3.10</td>
<td>0.21</td>
<td>4.19</td>
<td>0.35</td>
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<td>0.31</td>
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<td>$\epsilon_{\text{LUMO}}$ (47)</td>
<td>2.78</td>
<td>0.27</td>
<td>3.66</td>
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<td>2.59</td>
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<td>solids</td>
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<td>0.77</td>
<td>1.81</td>
<td>1.81</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

- The SC preserves the accuracy of $I$, $A$, and integer gaps, while it improves significantly on HOMO and LUMO energies, and derivative gaps
- S-MLDA predicts reasonable band gaps with consistent accuracy for systems of all sizes, ranging from atoms and molecules to solids
Band gaps of H-passivated Si nanocrystals

Computational details

- Systems under study: H-passivated spherical Si nanocrystals. The largest system is Si$_{191}$H$_{148}$ with a diameter of 20 angstrom.
- Geometries optimized by B3LYP with Lanl2dz ECP basis set, except that the largest system Si$_{191}$H$_{148}$ is optimized with semiempirical PM3 method.
- Diffusive basis functions are important to obtain accurate HOMO-LUMO gaps: 6-31G for H atoms; an sp-shell with an exponent of 0.0237 au and a d-shell with an exponent of 0.296 au added to Lanl2dz basis for Si atoms.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>d (Å)</th>
<th>basis</th>
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<tbody>
<tr>
<td>Si$<em>{29}$H$</em>{36}$</td>
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<td>Lanl2dz–spd</td>
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<tr>
<td>Si$<em>{35}$H$</em>{36}$</td>
<td>10.9</td>
<td>Lanl2dz–spd</td>
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<tr>
<td>Si$<em>{47}$H$</em>{60}$</td>
<td>11.8</td>
<td>Lanl2dz–spd</td>
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<tr>
<td>Si$<em>{71}$H$</em>{84}$</td>
<td>13.3</td>
<td>Lanl2dz–pd</td>
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<tr>
<td>Si$<em>{87}$H$</em>{76}$</td>
<td>14.1</td>
<td>Lanl2dz–pd</td>
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<td>Si$<em>{99}$H$</em>{100}$</td>
<td>15.4</td>
<td>Lanl2dz–pd</td>
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<td>Si$<em>{123}$H$</em>{100}$</td>
<td>16.1</td>
<td>Lanl2dz–d</td>
</tr>
<tr>
<td>Si$<em>{191}$H$</em>{148}$</td>
<td>19.4</td>
<td>Lanl2dz–d</td>
</tr>
</tbody>
</table>
Band gaps of H-passivated Si nanocrystals

The S-MLDA HOMO-LUMO gaps agree well with the GW gaps.
A Local Scaling Correction for Reducing Delocalization Error in Density Functional Approximations

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FIG. 1. (a) The local fractional occupation number $n(r)$ and (b) the local fractional orbital density $d(r)$ of a dissociating $\text{H}_2^+$ along the bonding axis at various internuclear distances $R$. A proton locates at $x = 0$, while the other proton resides
Local Scaling Correction

- **Motivation**
  - Consider $M^{0.5+}$ (M is an atom)
  - Diagonize PS matrix

  \[ \begin{bmatrix}
    1 & \vdots & 0 & 0 \\
    \vdots & 1 & 0.5 & 0 \\
    0 & 0 & 0 & \vdots \\
    0 & \vdots & 0 & 0 \\
  \end{bmatrix} \]

- $PS \rightarrow \begin{bmatrix}
    1 & \vdots & 0 & 0 \\
    \vdots & 1 & 0.5 & 0 \\
    0 & 0 & 0 & \vdots \\
    0 & \vdots & 0 & 0 \\
  \end{bmatrix}$

- $PS - (PS)^m \rightarrow \begin{bmatrix}
    1 & \vdots & 0 & 0 \\
    \vdots & 1 & 0.5 & 0 \\
    0 & 0 & 0 & \vdots \\
    0 & \vdots & 0 & 0 \\
  \end{bmatrix}$
Local Scaling Correction

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\[
\begin{align*}
\text{• } PS & \quad \rightarrow \\
\begin{bmatrix}
1 & \vdots & 0 & 0 \\
\vdots & 1 & 0.5 & 0 \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
\end{bmatrix}
\end{align*}
\]

\[
\begin{align*}
\text{• } PS - (PS)^m & \quad \rightarrow \\
\begin{bmatrix}
1 & \vdots & 0 & 0 \\
\vdots & 1 & 0.5 & 0 \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
0 & 0 & 0 & \ddots \\
\end{bmatrix}
\end{align*}
\]
Local Scaling Correction

- Motivation
  - $S \Rightarrow S_v$ (screened $S$ to reflect locality)
  - In atomic basis representation,

  $$l(r) = \lim_{m \to \infty} \chi^T(r)[P - (PS_v)^{m-1}P]\chi(r),$$

  $$d(r) = \lim_{m \to \infty} \chi^T(r)[I - (PS_v)^m - (I - PS_v)^m](S_v)^{-1}\chi(r),$$

- Our key idea
  - Apply local linearity condition using $f(r)$ and $d(r)$
Local Scaling Correction

- Correction functional

\[
\Delta E^{LSC-LDA} = -C_x \sum \int \left\{ l^\sigma(r) \left[ d^\sigma(r) \right]^\frac{1}{3} - \left[ l^\sigma(r) \right]^\frac{4}{3} \right\} dr \\
+ \frac{1}{2} \sum \int l^\sigma(r) u(\mu |r - r'|) \left[ d^\sigma(r') - l^\sigma(r') \right] \frac{drdr'}{|r - r'|} \\
- \frac{1}{2} \sum \int l^\sigma(r) w(|r - r'|) l^\sigma(r') \frac{drdr'}{|r - r'|},
\]

\(u(x)\) is a short-range function, \\
\(w(r)\) is a mid-range function, \\
\(w(x) = u(\mu_1 x) - u(\mu_2 x)\).
FIG. 2. Dissociation energy curves of (a) $\text{H}_2^+$ and (b) $\text{He}_2^+$. 
• Polarizability (longitudinal)

\[
\begin{array}{c}
\text{Hydrogen chain} \\
(H_2)_n
\end{array}
\]

\[
\begin{array}{c}
\text{2.0 a.u.} \\
\text{4.5 a.u.}
\end{array}
\]
Results

- Polarizability (longitudinal)

Polyethylene (PY)

\[ \text{H(C}_2\text{)}_n\text{H} \]
• Polarizability (longitudinal)

Polythiophene (PT)

$\text{H(C}_4\text{H}_2\text{S)}_n\text{H}$
Results

- $\text{OH}(\text{H}_2\text{O})_n$